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Fischer–Tropsch reactions and the environment

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Abstract

Suitable economic conditions given, the Fischer–Tropsch (FT) process is an alternative route to liquid fuels and chemicals (in particular linear 1-alkenes). Being S and N free and low in aromatics, the fuels are more environment friendly than those produced from crude oil. In particular, the production of environment friendly high quality diesel fuel is an attractive application of the FT process. Relatively large amounts of CO₂ are produced in the gasification processes, but whether this will really contribute to global warming is a disputed question. The water effluent from an FT complex is zero. ©1999 Elsevier Science B.V. All rights reserved.

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1. Carbon sources and reserves

The Fischer–Tropsch (FT) process converts a mixture of CO and H₂ (syngas) to a range of hydrocarbons. It can hence be considered as an alternative to crude oil for the production of both liquid fuels (gasoline and diesel) and chemicals (in particular, 1-alkenes).

The bulk of the world's energy, liquid fuels and chemicals, will presumably remain carbon based. Table 1 gives a rough comparative estimate of the recoverable sources of carbon [1].

Clearly, the reserves of coal exceed, by far, the sum of all alternative carbon sources, and in the long term, coal may well, due to lack of alternatives, return to the dominant position it held less than a century ago. In the shorter term, natural gas (methane) will be preferred to coal for both economic and environmental reasons.

It has been estimated that by the year 2015 oil will account for 38%, methane for 26% and coal for 25% of the world energy demand [2].

2. Viability of the FT process

To convert coal or methane to liquid fuels and chemicals via the FT process, it is necessary to first convert these carbon sources to syngas. Methane can be reformed to syngas with steam and oxygen, either thermally or catalytically. In the latter, more common approach, both primary (tubular) and secondary (autothermal) catalytic reformers are employed. Coal can be converted to syngas in non-catalytic gasifiers which vary from fluidised to moving bed types. The world's largest FT operator, Sasol, uses Lurgi moving bed gasifiers. Since the catalysts used in the downstream FT process are very sensitive to sulphur poisoning, the syngas must be purified to a high degree.

The production of syngas from methane or coal is highly endothermic and also the most expensive operation of the overall process. It accounts for about 70% of the capital and running costs of the total plant [1]. For FT to be competitive with crude oil, while the latter is still available, the cost of coal or methane needs to be low. It has been estimated that, based on methane, the FT route to fuels can be viable when the

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Table 1
Recoverable energy

Source	Reserve (10^9 bbl oil equivalent)	Life (years) ^a
Tar sands	1500	40
Oil	2000	50
Shale oil	2500	65
Gas (methane)	3000	75
Coal	53000	1300

^a At an annual energy demand of about 40×10^9 bbl oil per year.

price of crude oil exceeds about US \$16 per barrel [3]. As the price of crude is, at the time of writing, in the vicinity of US \$10 per barrel, the FT process can at present only be justified for very special economic, political or environmental reasons.

Many large crude oil deposits are associated with natural gas and it remains to be a common practice to flare the gas. This, however, is strongly being discouraged and so there is an incentive to utilise this gas, e.g. as pipeline gas. Long distance piping is too expensive and when the pipeline has to pass through countries other than the end consumer's, it also becomes politically hazardous. Liquifying the gas and then transporting it in specially designed tankers also becomes uneconomical beyond a certain distance. For such cases, converting the gas to liquid products and then shipping the liquid in normal tankers is being considered.

The practical thermal efficiencies of producing liquid fuels from methane are as follows [1]:

MTG gasoline	58%
FT diesel fuel	63%
CH ₃ OH	72%

(MTG is Mobil's process of converting methanol to gasoline.) As expected, the efficiencies increase with the H/C ratio of the product. Drawbacks of introducing methanol as a fuel include required design changes to engines, the solubility of water in methanol and the need for duplication of the fuel distribution networks during the period over which methanol will have to be phased in.

3. Carbon dioxide emission

When liquid fuel produced from crude oil is combusted, all the carbon in the fuel will be converted to

CO₂. If the oil is produced from methane via the FT process, then only about 75% of the carbon in CH₄ ends up in the FT products, and the balance is converted to CO₂. After combustion of the FT fuel, it means that, overall, for the same amount of hydrocarbon combusted, 33% more CO₂ is released into the atmosphere. As coal has a low hydrogen content, the situation is worse. In a typical coal based FT operation, about 33% of the mined coal is used to raise steam and the remaining 67% is fed into the gasifiers where about 50% of this coal is burnt to give CO₂ (to generate the energy required by the highly endothermic gasification reaction). The overall situation after combustion of the FT oil is that about 200% more CO₂ is released into the atmosphere than in the case of the equivalent amount of crude oil derived fuel.

As CO₂ is one of the so-called greenhouse gases, there is considerable pressure, much of it simply 'political', to minimise CO₂ emission. Now, if the 'greens' are correct, then the FT process, particularly if based on coal, would be an undesirable way of producing liquid fuels and chemicals when the crude oil reserves are depleted eventually. The theory, however, that increased CO₂ levels would lead to global warming with concomitant disasters is strongly questioned by many scientists. It is shown that despite increased CO₂ levels, global average temperatures have actually cooled slightly over the past two decades. Over the past 100 years, both the global average temperature and the atmospheric CO₂ content have increased, but the temperature rise has preceded the CO₂ rise suggesting that the latter cannot be the cause of the former [4]. Cyclic long term changes in the temperature are well documented, e.g. the 'medieval climate optimum' 1000 years ago and the 'little ice age' of 300 years ago. Thus, the present upward trend could simply be part of the normal long term cycle.

4. Process options for the FT synthesis route

In commercial practice, there are two modes of operations, the low temperature FT process (LTFT) which is geared at high wax production and the high temperature (HTFT) process which is geared mainly at producing alkenes and gasoline [1,3].

Currently the most efficient reactor type for the LTFT is the slurry reactor in which syngas is passed

upwardly through a slurry consisting of catalyst particles suspended in molten FT wax. The operating temperature depends on whether the catalyst is cobalt or iron based, but is usually below 250°C in order to minimise unwanted methane production and to maximise wax selectivity. Another reason for avoiding high temperatures is the desire to minimise wax hydrocracking. The HTFT process operates with an iron based catalyst at about 350°C with the syngas passing through a fluidised bed of finely divided catalyst. Low temperatures cannot be used as the two phase system (gas and catalyst) would be defluidised due to the formation of liquid waxes. On account of the high temperature, the catalyst in the HTFT process is much more active than it is in the LTFT process and so the gas throughput and hydrocarbon production rate is much higher.

Since both reactor types are operated in a fluidised mode, the rate of heat exchange into the immersed coiling coils is very high, resulting in near isothermal conditions. In fluidised bed reactors, the addition of fresh catalyst and the removal of deactivated catalyst is carried out on-line, which results in long reactor runs. These reactors are also much cheaper to construct than their predecessors, namely the multitubular fixed bed reactors for LTFT and the circulating fluidised bed reactors for the HTFT [1]. All these improvements have translated to more efficient conversion of the expensive syngas.

Table 2 indicates typical selectivities obtained with iron based catalysts for the LTFT and HTFT processes.

5. Composition of the FT products

The hydrocarbons produced in the FT process are predominantly linear, and furthermore, the alkenes are predominantly 1-alkenes (see Table 2). The high 1-alkene content is advantageous for the production of chemicals (see Section 8), while the linearity of the hydrocarbon chains significantly influences the quality of the diesel and the gasoline (see Sections 6 and 7). Besides hydrocarbons, the FT reaction also produces lesser but significant amounts of oxygenated compounds, namely alcohols, aldehydes, ketones and acids [5]. Since the production of ketones and aromatics at low temperatures is very low and their selectivities increase with increasing temperature, it appears that ketones and aromatics are secondary products [5].

Table 2
Typical FT products spectra with iron catalysts

	235°C (LTFT)	340°C (HTFT)
<i>Selectivities (C atom%)</i>		
CH ₄	3	8
C ₂ H ₄	0.5	4
C ₂ H ₆	1	3
C ₃ H ₆	1.5	11
C ₃ H ₈	1.5	2
C ₄ H ₈	2	9 (85% 1-butene)
C ₄ H ₁₀	2	1
C ₅ –C ₆	7	16
C ₇ – 160°C	9	20
160–350°C	17.5	16
+350°C	51	5
Oxygenates	4	5
<i>% Breakdown</i>		
C ₆ cut		
<i>n</i> -Hexane		8
1-Hexene		58
Methyl 1-pentenenes		24
C ₁₀ cut		
<i>n</i> -Decane		8
1-Decene		38
Methyl 1-nonenes		20
C ₅ –C ₁₂ cut		
% Total alkanes	29	13
% Total alkenes	64	70
% Aromatics	0	5
% Oxygenates	7	12

Since all sulphur compounds are removed upstream of the FT reactors, the FT products are sulphur free. The products are also free from nitrogen compounds, and hence, the FT fuels themselves make no contribution to the formation of NO_x gases in combustion engines.

6. Production of diesel fuels

Typically, the efficiency of a diesel fuelled engine is about 44% as against about 24% for a gasoline engine. From an overall environmental point of view, the use of diesel, therefore, should be preferred.

6.1. The LTFT process

The LTFT process is best suited for the production of large quantities of high quality diesel fuel.

On account of the linearity of the hydrocarbons, the straight-run diesel cut has a cetane number of about 75. Presently, the required cetane number in the market place varies from 40 to 50. The selectivity of the straight-run diesel is, however, only about 18%. Heavier than diesel cuts, i.e. the waxes, which account for about 51% of the total products, can readily be hydrocracked under mild conditions to yield about 80% diesel, 15% naphtha and 5% C_1 – C_4 gas. The cetane number of this secondary diesel is still very high and the combined diesel has a cetane number of about 73. The overall final diesel to naphtha ratio is about 2.4 : 1.

This route to diesel production was investigated on pilot plant scale in the Sasol Research division in the mid 1970's and published subsequently [5,6]. At that time, the diesel specifications were not as stringent as at present and also the production of gasoline was a more profitable process, and thus, this LTFT route to diesel was not pursued. In recent years, however, there has been a revived interest in this route to high quality diesel fuel and both Exxon and Sasol now offer processes based on the LTFT slurry reactors. The Shell FT plant in Malaysia which came on stream in 1993 uses multitubular fixed bed reactors to produce wax and also offers diesel produced via the mild hydrocracking of wax.

Tests carried out with the diesel produced via the Sasol process have shown that it is readily biodegradable. It has a cetane number of 74 as against 40 for conventional US diesel fuel. The aromatic content is about 2 mass% as against about 32% in US diesel fuel. The emission levels for hydrocarbons, CO , NO_x and particulate matter (PM) were, respectively, 56, 33, 28 and 21% lower [7].

The light naphtha produced in this process is free from aromatics and has a high linear alkane content, and thus, without further catalytic processing, it is not suitable as gasoline. However, it is an excellent candidate for naphtha cracking [6]. Higher yields of light alkenes are derived compared to the usage of petroleum derived naphtha. Thus, the ethylene production is more efficient.

6.2. The HTFT process

On account of the higher operating temperature, the hydrocarbons are more branched, and consequently,

the cetane number of the straight-run FT diesel is about 55 [5]. The HTFT process does, however, produce large amounts of light alkenes (see Table 2) and the C_3 – C_5 alkenes can be oligomerised using the shape selective ZSM-5 catalyst to yield a diesel with a cetane number of about 50. (Oligomerisation being an acid catalysed reaction would normally produce a highly branched product, and thus, a low cetane number diesel, but the shape selectivity of the ZSM-5 catalyst ensures that branching is minimised. Overall, the final ratio of the diesel produced to the naphtha produced would be about 1 : 1.

On account of the lower cetane number of the diesel and the lower diesel/naphtha ratio, the HTFT process is inferior to the LTFT process as far as producing high quality diesel is concerned.

7. Production of gasoline

Of the two FT processes discussed in Section 4, the HTFT one is by far the better option for the production of gasoline. Not only is the conversion capacity of the reactor type much higher than that of the LTFT reactors but also the gasoline selectivity is higher and it has a higher octane rating.

In recent years, there has been a move towards lower alkene and lower aromatic contents as well as lead free gasoline. To compensate for the resultant lower octane rating, various ethers such as MTBE and TAME are being added to gasoline. The ideal 'environment friendly' gasoline would consist of predominantly branched alkanes (e.g. isooctane).

The benzene content of HTFT gasoline is very low and the total aromatic content is about 5% which is well below the presently prescribed limits. The alkene content, however, at about 70%, is far too high. The straight-run C_5/C_{10} FT cut could be hydrogenated and the C_5/C_6 cut isomerised by, for example, the UOP Penex process, while the C_7/C_{10} cut could be platinum reformed.

As the C_3/C_4 alkene production is high (see Table 2), additional gasoline could be produced by oligomerising these alkenes over non-selective acid catalysts, followed by hydrogenation to yield branched alkanes.

The HTFT process produces very little methanol [5] and only a limited amount of isoalkenes, and so,

the scope for the production of the ether MTBE or ETBE is limited. The availability of large amounts of propene, however, makes the production of di isopropylether (DIPE) feasible, which is as good an octane booster as the other ethers [8].

As is clear from the foregoing, a large number of catalytic process steps is required to produce a high octane, environment friendly gasoline via the FT process. It is for this reason that the production of high quality diesel via the LTFT process is rather recommended as it involves fewer process steps.

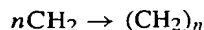
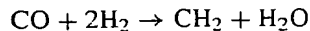
8. Production of chemicals

In South Africa, the total industrial need for ethene and propene, for the production of polyethylene (PE), polyvinyl chloride (PVC), polypropylene (PP) and acrylonitrile are supplied by the Sasol HTFT process. Whereas the co-monomers C_4 , C_6 and C_8 1-alkenes required for the production of the various grades of PE are normally produced by ethene oligomerisation, these products are of course present in large amounts in the FT product streams (see Table 2). At present, Sasol extracts and purifies large tonnages of 1-hexene for export. 1-Octene will also be produced in the near future.

The longer chain 1-alkenes present in the heavier HTFT oil cuts can selectively be converted to linear primary alcohols by hydroformylation with homogeneous cobalt complexes. Since the alcohols formed have much higher boiling points than the feed hydrocarbon cuts, they are separated easily, and so, little or no purification of the raw FT cuts needs be carried out. The linear C_{12} – C_{14} alcohols, used for the production of detergents, are normally produced from natural oils, e.g. palm oil, and so, this makes the viability of the application of these particular FT oil cuts independent of the price of crude oil.

Whereas the HTFT process produces predominantly shorter chained linear alkenes, the LTFT process produces predominantly linear longer chain alkanes. After catalytic hydrofining, these linear alkanes ranging from liquids to long chain waxes are sold as chemicals, fetching much higher prices than they would as fuels.

The FT reaction can be seen as the polymerization of units of ' CH_2 ' which are formed on the surface of the FT catalyst.



Hence, the FT reaction produces large amounts of water since for every bound carbon atom, a molecule of water is produced. On leaving the FT reactors, the bulk of the lower molecular mass alcohols, aldehydes, ketones and acids will, after condensation, remain dissolved in the liquid water phase (the heavier oxygenates are dissolved in the liquid oil phase). At the Sasol plants, the bulk of the oxygenated compounds are extracted from the water phase refined and marketed.

In the Sasol coal based FT plant, excess steam has to be fed into the coal gasifiers and it is condensed downstream. This water (gas liquor) contains dissolved phenols, cresols and ammonia. These are extracted, refined and marketed. The raw syngas from the coal gasifiers contains about 1% H_2S (the actual level depends on the quality of coal). The H_2S together with the CO_2 is extracted by the Rectisol process [5] and the H_2S is then converted to elemental sulphur by the Sulfreen process.

9. Water management

With effective control, there need be no water effluent leaving an FT complex. The normal rain run-off water, the FT product water containing any unextracted oxygenates (see Section 8), and in the case of a coal based plant, the stripped raw gas liquor (see Section 8), are treated in an aerobic bioworks where all the organic material is oxidised biologically. The biological sludge produced is incinerated. The treated water is used as cooling water in the FT complex. The cooling water system blowdown stream containing inorganic salts is evaporated, and/or, in the case of a coal based plant, treated with the coal ash which binds the salts chemically. For a CH_4 based FT plant, the FT water and run-off water can be treated anaerobically to produce methane.

References

- [1] M.E. Dry, *Appl. Catal. A: Gen.* 138 (1996) 319.
- [2] P. Davies, in: *Proceedings of the 11th World Clean Air Congress*, Durban, South Africa, September 1998.
- [3] B. Jager, *Natural Gas Conversion IV, Studies in Surface Science and Catalysis*, vol. 107, Elsevier, Amsterdam, 1997, p. 219.
- [4] A.B. Robinson, S.L. Baliunas, W. Soon, Z.W. Robinson, *Medical Sentinel* 3(5) (1998) 171.
- [5] M.E. Dry, in: B.E. Leach (Ed.), *Applied Industrial Catalysis*, vol. 2, Academic Press, New York, 1983, Chapter 5.
- [6] M.E. Dry, *Hydrocarbon Processing*, 1982, p. 121.
- [7] P.W. Schwaberg, I.S. Myburgh, J.J. Botha, P.N. Roets, L.P. Dancuart, in: *Proceedings of the 11th World Clean Air Congress*, Durban, South Africa, September 1998.
- [8] F. Heese, M.E. Dry, K.P. Möller, *Catal. Today* 49 (1999) 327.